The Electronic Polarizability of Polymethines†

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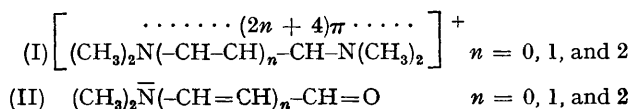(*Zentralinstitut für Optik und Spektroskopie der Deutschen Akademie der Wissenschaften zu Berlin, DDR* 1199 *Berlin, Rudower Chaussee, German Democratic Republic*)

Summary The relative π-electronic polarizabilities of ideal polymethines are essentially higher than those of comparable aromatic or polyene-like compounds; unsymmetrical merocyanines have the same polarizabilities as polymethines in polar solvents but polarizabilities similar to those of polyenes in non-polar solvents.

† For our previous paper on problems of solvatochromism, see ref. 1. These results were presented at the VI. International Conference on Photochemistry, Bordeaux 1971, and are part of the thesis of K.-D. Nolte, DAW, Berlin 1972.

UNSATURATED organic compounds in the ideal polymethine state have unique features.[2] For instance they are usually strongly coloured and should have large electronic polarizabilities. However, it has been assumed until now that the polarizabilities of polymethines have the same order of magnitude as those of aromatic or polyene-like compounds; for example, with dipole measurements[3] or with theories of solvatochromism.[4] Furthermore, it was generally believed that the influence of solvents on the polarizability of organic compounds could be neglected.

Since it is very difficult to determine experimentally the polarizability of strongly coloured substances we have measured the molar refractions and the dispersion in the visible spectral range of the simplest polymethine cyanine ions (I) and polymethine merocyanines (II) (vinylogues of formamide) in different solvents.

$$(I) \begin{bmatrix} \cdots\cdots(2n+4)\pi\cdots\cdots \\ (CH_3)_2N(-CH-CH)_n-CH-N(CH_3)_2 \end{bmatrix}^+ \quad n = 0, 1, \text{ and } 2$$

$$(II) \quad (CH_3)_2\overline{N}(-CH=CH)_n-CH=O \qquad n = 0, 1, \text{ and } 2$$

These substances possess a polymethine-like structure, but absorb at relatively short wavelengths.[5] The polarizabilities were calculated from these measurements both on the basis of the Lorentz function and on the basis of the Onsager theory, taking into account corrections for the solvent field.[6] However, the results do not differ markedly.[7]

For the comparison of polarizabilities of different compounds we have calculated the relative π-electronic polarizability $\bar{\alpha}_\pi(h)$ within homologous series, defined as follows:

$$\bar{\alpha}_\pi(h) = \bar{\alpha}(h) - [\bar{\alpha}(1) + \Delta\bar{\alpha}_\sigma]$$

where $\bar{\alpha}(h)$ is the measured average polarizability of a particular compound ($h = 2, 3, \cdots$) of a homologous series. $\bar{\alpha}(1)$ is the measured average polarizability of the first reference compound of this series and $\Delta\bar{\alpha}_\sigma$ is the average σ-electronic polarizability of the structure element, which has been added to the first reference compound ($h = 1$) of a homologous series to build up a particular compound ($h = 2, 3, \cdots$). In the case of polymethines, this structure element represents one or more vinylene groups, which each group contributes two π-electrons. We estimated the σ-polarizability $\Delta\bar{\alpha}_\sigma$ of one vinylene group to be $23{\cdot}54 \times 10^{-25}$ cm^3 from the longitudinal and the transverse portions taken from an increment system.[8] In the same way we estimated a value of $52{\cdot}27 \times 10^{-25}$ cm^3 for the σ-polarizability of one cis-butadienyl group in the case of the linear condensed aromatic compounds.

In the Figure, the values determined for the relative π-electronic polarizabilities $\bar{\alpha}_\pi(h)$ are shown as a function of additional π-electrons. The numerical values of $\bar{\alpha}(1)$ for the first reference compounds in methanol amount to $124{\cdot}7 \times 10^{-25}$ cm^3 for the cyanine (I; $n = 0$) and to $81{\cdot}4 \times 10^{-25}$ cm^3 for dimethylformamide (II; $n = 0$) on the basis of the Onsager theory. The experimental values for the aromatic compounds (benzene, naphthalene, and anthracene)
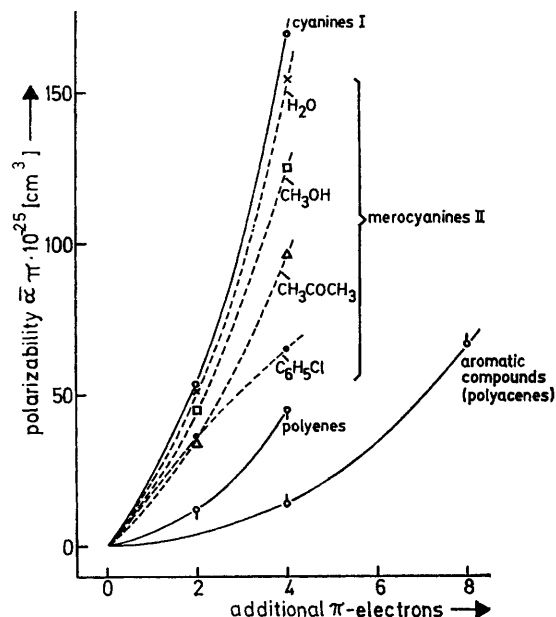

FIGURE. Relative π-electronic polarizability $\bar{\alpha}_\pi$ of unsaturated compounds with increasing number of π-electrons. The solvents of the merocyanines (II) are indicated on the curves.

were taken from the literature.[9] The values for the polyenes (butadiene, hexatriene, and so on) were calculated by the method described in ref. 10, and are in good agreement with other experimental results.

Two essential conclusions can be drawn from our results: (1) the π-polarizabilities of cyanines in the polymethine state are essentially higher than those of polyene-like or aromatic substances with the same number of π-electrons; (2) whereas the polarizability of the cyanines does not show solvent-dependence,[7] the π-polarizability of merocyanines can be varied by the polarity of the solvent between that of polyene-like compounds in non-polar solvents and that of polymethine-like compounds in polar solvents.

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